DALTON COMMUNICATION

Structure and magnetic properties of $Mn^{II}[N(CN)_2]_2$(pyrazine). An antiferromagnet with an interpenetrating 3-D network structure

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Received 6th October 1998, Accepted 7th October 1998

$Mn[N(CN)_2]_2$(pyz) (pyz = pyrazine) orders antiferromagnetically at low temperature and possesses intralayer μ-NCNCN and interlayer μ-pyz ligands that form a pseudo-ReO_3 interpenetrating network structure.

The synthesis of multidimensional network structures is at the forefront of modern research due to their ability to design as well as control a wide range of architectures.[1] Likewise, the study of molecule-based magnets due to their potential for exhibiting cooperative magnetic behavior is being widely investigated.[2] Polydentate cyanocarbons have been utilized extensively to assemble transition metals into 1-, 2- and 3-D arrays.[3] Tetracyanoethylene, TCNE, has been used to link Mn(porphyrin) into 1-D chains[4] and when reacted with $V(C_6H_6)_2$ yields a 3-D polymeric ferrimagnet with a critical temperature far exceeding room temperature.[5] Work has focused on diamagnetic $[N(CN)_2]^-$ due to its ability to bond to multiple transition metal sites.[6] Tricoordinate dicyanamide forms rutile-structured ferromagnets with Co^{II} and Ni^{II} with T_c's ranging from 9 K (Co) to 21 K (Ni) while isostructural Mn^{II} orders antiferromagnetically below 16 K.[7,8] In addition to $M[N(CN)_2]_2$ complexes, octahedral complexes of $M[N(CN)_2]_2L_2$ (L = Lewis base) stoichiometry can be prepared. Owing to the polydentate character of $[N(CN)_2]^-$ numerous structural motifs can be constructed. Herein we report the single crystal structure and magnetic properties of $Mn^{II}[N(CN)_2]_2$(pyz) (pyz = pyrazine).

Reaction of $MnCl_2$, $Na[N(CN)_2]$, and pyrazine in H_2O–EtOH results in the formation of small pale yellow crystals of $Mn^{II}[N(CN)_2]_2$(pyz)† whose structure was solved by X-ray diffraction.‡ The structure consists of infinite MNCNCNM-linked $Mn[N(CN)_2]_2$ layers bridged by pyrazine affording pseudo-cubic frameworks, Fig. 1, similar to ReO_3. Furthermore, owing to the combination of the large separation between Mn atoms and the small ligand sizes, large cavities are formed which can accommodate a second interpenetrating lattice.

Each octahedral Mn^{II} is bonded to four different $[N(CN)_2]^-$ ligands in the *ab*-plane and two different pyrazine bridges along *c*. Each $[N(CN)_2]^-$ is μ-bonded to two Mn^{II}'s through the terminal CN's. The Mn^{II} octahedron is tetragonally elongated from O_h symmetry with Mn–N distances ranging from 2.173(7) Å (dicyanamide N's) to 2.299(9) Å (pyrazine N's) and average 2.236 Å while *cis*-N–Mn–N′ bond angles range from 83.5(3) to 92.3(6)°. The dicyanamide ligand displays nearly ideal C_{2v} symmetry with C≡N bond distances averaging 1.145 Å typical for this ligand.[9] The C≡N–Mn bond angles deviate appreciably from linearity and range from 142.6(9) to 164.9(13)°. The intranetwork Mn···Mn separations are 7.351 (through the pyrazine bridge), 8.678, and 8.803 Å, which exceed the shortest Mn···Mn internetwork separation of 6.282 Å. For comparison, $Zn[N(CN)_2]_2$ features a 2-D layered structure with only μ-N≡C linkages similar to $Mn[N(CN)_2]_2$(pyz), however due to the tetrahedral Zn^{II} centers, the layers are markedly buckled and pack in a staggered fashion.[10] The pyrazine ligands reside in noncoplanar orientations with a dihedral angle of 43.1° relative to the "cube" faces. Thermogravimetric analysis reveals a sharp weight loss at ≈230 °C corresponding to the loss of one pyrazine per formula unit (Calc. 30.0; obs. 29.9). To the best of our knowledge this is the only structurally characterized unsubstituted pyrazine Mn^{II} complex.

Several 2-D materials such as $Co(pyz)_2(NCS)_2$ feature μ-pyz ligands that organize paramagnetic metal centers into square grids.[11] Interestingly, the only example of a 3-D network solid consisting of pyz bridges is diamagnetic $[Ag(pyz)_3][SbF_6]$ which also possesses a ReO_3-like structure.[12]

The 2 to 300 K temperature dependence of the magnetic susceptibility, χ, of $Mn[N(CN)_2]_2$(pyz) was measured and fit by the Curie–Weiss expression, $\chi \propto (T - \theta)^{-1}$, with $g = 2.01$ and $\theta = -3.6$ K indicative of finite antiferromagnetic coupling between the Mn^{II} metal sites, Fig. 2. At 300 K the effective moment is 5.90 μ_B, in excellent agreement with the expected value (5.92 μ_B) for isolated $S = 5/2$ Mn^{II} ions and due to antiferromagnetic coupling decreases at lower temperature. A similar material, $Mn[N(CN)_2]_2(py)_2$, also has μ-NCNCN bridges and weaker antiferromagnetic coupling is observed ($\theta = -1.8$ K) suggesting enhanced spin coupling *via* the pyrazine linkages.[13] To elucidate the exchange coupling through the NCNCN and pyz linkages, χ was also fit to a 2-D (χ_{2D}) antiferromagnet model derived by Rushbrooke and Wood[14a] with $g = 2.01$ and $J/k_B = -0.18(1)$ K.[14b] To account for the residual 3-D interactions an additional mean-field correction (χ_{MF})[14c,d] was included, eqn. (2), also with $g = 2.01$ and $J'/k_B = -0.21(1)$ K.

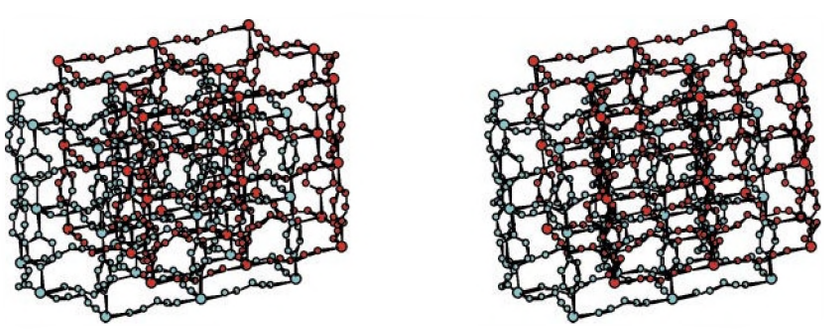

Fig. 1 Stereoview of the crystal structure of $Mn^{II}[N(CN)_2]_2$(pyz) illustrating the interpenetrating pseudo-ReO_3 frameworks.

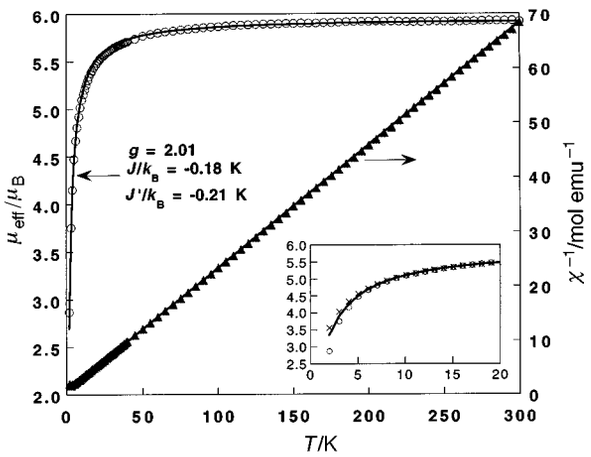

Fig. 2 Temperature dependence of and effective magnetic moment (μ_{eff}) and the reciprocal molar magnetic susceptibility (χ^{-1}) for $Mn^{II}[N(CN)_2]_2(pyz)$. The data was fit to the expression derived by Rushbrooke and Wood[14a] for a 2-D antiferromagnet (——) with $S = 5/2$, $g = 2.01$ and $J/k_B = -0.18$ K. Interlayer exchange was determined to be $J'/k_B = -0.21$ K. A low temperature comparison to the Curie–Weiss law (×) with $g = 2.01$ and $\theta = -3.6$ K is also shown (inset).

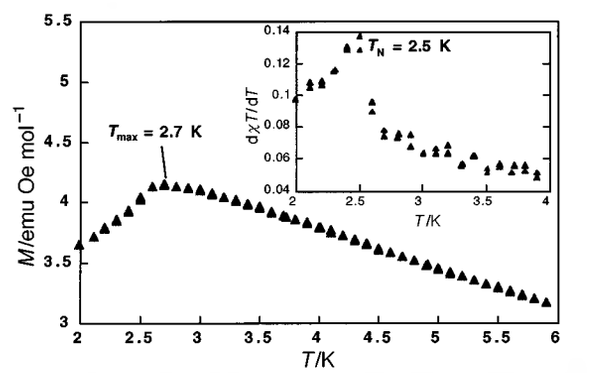

Fig. 3 Zero-field and field-cooled magnetization as a function of temperature for $Mn^{II}[N(CN)_2]_2(pyz)$ taken in a 50 Oe applied dc magnetic field on warming. $T_N = 2.5$ K as determined from the plot of $d\chi T(T)/dT$, inset.

$$\chi_{2D} = \frac{2.91Ng^2\mu_B{}^2}{k_BT[1 + C_1x + C_2x^2 + C_3x^3 + C_4x^4 + C_5x^5 + C_6x^6]} \quad (1)$$

$$\chi_{MF} = \frac{\chi_{2D}}{[1 - \chi_{2D}(2zJ'/Ng^2\mu_B{}^2)]} \quad (2)$$

J is assigned to coupling within the layers *via* the NCNCN bridges and J' is assigned to coupling between the layers *via* the pyrazine bridges. The zero field splitting is typically negligible for high spin Mn^{II}[15] and is ignored. Evidence of long-range antiferromagnetic ordering is demonstrated by a cusp in $M(T)$ at 2.7 K, Fig. 3. The actual magnetic ordering temperature occurs just below the maximum and can be determined from a plot of $d\chi T(T)/dT$, Fig. 3 inset.[16] Additionally, zero-field and field-cooled magnetization experiments carried out in small applied magnetic fields ($H \leq 50$ G) fail to show bifurcation unlike α-$Mn[N(CN)_2]_2$.[8] Field-dependent magnetization measurements performed at 2 K to 5 T demonstrate behavior typical of an ordered antiferromagnet. The magnetization rises nearly linearly to approximately 19 000 emu Oe mol^{-1} (at 3 T) and then decreases reaching a final value of 26 600 emu Oe mol^{-1} (at 5 T). This value is only slightly less than the expected value of 27 925 emu Oe mol^{-1} expected for $S = 5/2$ Mn^{II}.

Acknowledgements

The authors gratefully acknowledge the ACS-PRF (Grant #30722-AC5) and the U. S. Department of Energy (Grant #DE-FG03-93ER45504) for support of this work.

Notes and references

† A 5 mL aqueous solution of $MnCl_2 \cdot 4H_2O$ (1.7 mmol, 0.3373 g) was mixed with a 1:1 H_2O–EtOH solvent mixture (10 mL) containing $Na[N(CN)_2]$ (3.4 mmol, 0.3034 g) and pyrazine (1.7 mmol, 0.1360 g) affording immediate precipitation of a pale yellow powder (90%). Small crystals suitable for X-ray diffraction were grown from the filtrate solution upon standing at room temperature for 2 weeks. ν_{CN} (Nujol): 2170s, 2180s, 2193s (sh), 2236m, 2248m, 2311m, 2325m and 2357w cm^{-1}.

‡ Crystal data for $C_8H_4MnN_8$: $M = 267.13$, monoclinic, $P2_1/n$, $a = 7.3514(11)$, $b = 16.865(2)$, $c = 8.8033(12)$ Å, $\beta = 90.057(2)°$, $U = 1091.4(3)$ Å^3, $Z = 4$, $D_c = 1.626$ Mg m^{-3}, μ(Mo-Kα) = 1.199 cm^{-1}, $T = 198(2)$ °C. Of 4518 data ($4 \leq 2\theta \leq 57°$), 1556 were independent ($R_{int} = 0.0928$), and 1019 were observed [$I > 2\sigma(I)$]. Two nitrogen atoms in two different cyano groups were positionally disordered 70:30 and 60:40. CCDC reference number 186/1201. See http://www.rsc.org/suppdata/dt/1998/3705/ for crystallographic files in .cif format.

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Communication 8/07788F